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EFFECTS OF RARE-EARTH ADDITIONS TO PHOSPHORUS-DOPED 2-1/4 Cr - 1 Mo STEELS

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EFFECTS OF RARE-EARTH ADDITIONS TO PHOSPHORUS-DOPED 2-1/4 Cr - 1 Mo STEELS

by

R.F. Knight*

ABSTRACT

The properties, inclusion contents and microstructures of phosphorus-doped, air and vacuum-melted 2-1/4 Cr - 1 Mo steels, with and without additions of rare-earths, are compared. Of these steels, high purity (low-phosphorus) steel had the best properties in the retoughened condition, and developed very little embrittlement when subjected to a step-cooling treatment. Rare-earth free, phosphorus-doped steels developed substantial embrittlement. Rare-earth additions resulted in a significant decrease in the degree of embrittlement, an effect that was twice as beneficial to vacuum-melted as to air-melted steel. However, the large rare-earth additions made, resulted in substantial increases in the number and volume fraction of inclusions and thus, a decrease in upper-shelf impact energy.

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LABORATOIRES DE RECHERCHE EN MÉTALLURGIE PHYSIQUE
RAPPORT MRP/PMRL 83-15(TR)

LES EFFETS DE L'ADDITION DE TERRE RARE AUX ACIERS 2-1/4 Cr - 1 Mo ENDUITS DE PHOSPHORE

par

R.F. Knight*

RÉSUMÉ

Le présent rapport compare les propriétés, les contenus d'inclusions et les microstructures des aciers 2-1/4 Cr - 1 Mo enduits de phosphore et fondus à l'air et sous vide, avec ou sans addition de terre rare. Parmi ces aciers, ceux d'une grande pureté (faible teneur en phosphore) présentaient les meilleures propriétés dans les conditions de renforcement, et ils n'ont développé que très peu de fragilisation lorsque soumis au traitement de refroidissement par étapes. Les aciers enduits de phosphore mais sous terre rare ont atteint un degré substentiel de fragilisation. Les additions de terre rare ont causé une baisse considérable du degré de fragilisation, et de façon deux fois plus efficace dans le cas des aciers fondus sous vide que dans celui des aciers fondus à l'air. Toutefois, la terre rare ajoutée en grande quantité a causé une augmentation considérable du nombre et du volume d'inclusions, et conséquemment une diminution de la résilience au palier supérieur.

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INTRODUCTION

The materials of choice for hydrogenation pressure vessel applications have generally been Cr-Mo steels. Such steels, when cooled slowly through the temperature range 575°C-325°C, or when exposed for prolonged periods to temperatures in this range, as in hydrogenation service, exhibit temper embrittlement (1). Such embrittlement occurs only in the presence of impurity elements such as antimony, phosphorus, tin and arsenic (2). For Cr-Mo steels, phosphorus appears to be the most deleterious element.

In tests to evaluate the susceptibility of 2-1/4 Cr - 1 Mo steel to temper embrittlement, a compositional factor $J = (Si+Mn)(P+Sn)\times10^4$, is found to be linearly related to the embrittlement that results from a step-cooling treatment (3). It has been reported (4) that the addition of rare-earth elements to a content which is the sum of 8.7S + 2.3Sn + 4.5P (all contents wt.%) prevents the development of temper embrittlement.

Previous PMRL research (5) evaluated the effect of rare-earth additions on a phosphorus-doped 2-1/4 Cr - 1 Mo steel. It was found that in this steel, which had been air-melted, the addition of rare-earths caused marked deterioration in impact toughness, and only partially suppressed temper embrittlement. The reduction in toughness was ascribed to the increase in volume fraction of inclusions from oxidation of the rare-earths and retention of RE oxides and oxy-sulphides in the cast steel.

The current research compares inclusion contents and mechanical properties of air melted 2-1/4 Cr - 1 Mo steels with vacuum melted steels of similar composition cast in a chamber back-filled with argon before additions of rare-earths were made.

PROCEDURE

SCOPE AND CODING

Three air-melted steels and two vacuum-melted steels are evaluated. These are coded, as follows:

A1 - Air-melt, normal Si, low P

A2 - Air-melt, high Si & P

A3 - Air-melt, high Si & P + RE

V1 - Vacuum-melt, high Si & P

V2 - Vacuum-melt, high Si & P + RE

These steels were evaluated in two conditions of heat treatment, embrittled (E) and retoughened (R). Most testing was conducted in an orientation longitudinal to the direction of rolling (L), with limited testing in the transverse (T) orientation.

MELTING

The air-melted steels were induction-melted under argon using electrolytic iron as the charge material and high-purity ferroalloys for alloy additions. Rare-earths were added as rare-earth silicide (RESi), wrapped in aluminum foil and plunged into the ladle immediately before pouring the 45 kg ingots.

The aim of the current work was to prevent oxidation of the rare-earths by vacuum-melting and to make the RESi addition and casting under argon protection. To this end, a master alloy was air-melted to a composition close to the target composition. A charge of 20 kg of master alloy and 32.9 g of FeMo was melted down under vacuum and the temperature raised to 1550°C. A small correcting addition of Cr was made (76.8 g of low-C FeCr) and the chamber backfilled with argon to 6700 mm pressure. The temperature was raised to 1600°C and ingot V1 was poured, with 60 g of FeSi wrapped in 9 g of aluminum foil suspended in the ingot mould at half-height. The last addition was required to match the Si content of the rare-earth addition. An addition of 9 g of aluminum and 90 g of RESi was made to the bath, and ingot V2 was poured. After cropping, these ingots yielded square-section billets slightly tapered from top to bottom, with a mid-length section 11 cm square and a length of 14 to 15 cm.

The chemical compositions of the experimental steels are given in Table 1.

FORMING

All the billets were soaked at 2300°C and rolled directly to 13 mm thick plates. These were cut to provide "E" and "R" sections for the two heat-treated conditions.

HEAT TREATMENT

All plate sections were austenitized at 925°C for 60 min and water-quenched, and then tempered at 675°C for 60 min and air-cooled. They were

then given a step-cooling embrittlement treatment, as follows:

595°C (1 h) + 540°C (15 h) + 525°C (24 h)
+ 495°C (48 h) + 470°C (72 h)
+ furnace-cool to 315°C
+ air-cool to room temperature

One plate section of each steel was then designated as "E" for the embrittled condition and received no further treatment. The remaining plate section of each steel was tempered at 650°C for 30 min and water-cooled, and designated "T" for the retoughened condition.

EXPERIMENTAL RESULTS

TENSILE TESTING

Tensile properties were determined for the vacuum-melted steels only, for both E and R conditions. The results, shown in Table 2, are averages of duplicate tests using specimens with a gauge diameter of 4.55 mm.

IMPACT TESTING

Impact properties were determined by measuring the energy absorbed (J) while breaking Charpy V-notch specimens at various testing temperatures. The results are recorded in Table 3.

Impact curves were obtained from these data. The curves are presented with the data points eliminated for the sake of clarity. Curves for the retoughened (R), longitudinal (L) samples are shown in Fig. 1, whereas those for the embrittled (E), longitudinal (L) samples are presented in Fig. 2. Figure 3 compares longitudinal (L) and transverse (T) orientations for the vacuummelted steels.

The effects of chemical differences, rare-earth additions vacuum-melting, embrittlement heat treatment and sample orientation are all apparent from direct comparison of the curves in Figs. 1 to 3. For example, the comparison of the "L" and "T" curves in Fig. 3 illustrates the effects of sample orientation. However, to facilitate comparison, curves showing the changes in transition temperature (ΔTT) at particular energy levels have been derived from the impact curves.

Figure 4, which compares A2RL with A1RL, illustrates the large increase in transition temperature caused by high levels of P and Si in all the

experimental steels except A1. Figure 5 illustrates the improvement in transition temperature resulting from vacuum-melting rather than air-melting. Figure 6 shows the increase in transition temperature resulting from the addition of rare-earths, and Fig. 7 shows the net increase in transition temperature from the combined effects of vacuum-melting and rare-earth additions.

It should be noted that the addition of rare-earths, besides causing an increase in transition temperature, as illustrated in Fig. 6, also results in a significant decrease in the upper-shelf energy. Comparison of the impact curves in Fig. 1 shows that this decrease is greater for the vacuum-melted steel than for the air-melted steel. Vacuum-treatment of the RE-free steel improves the upper shelf, but it has no effect on the upper shelf of the RE-bearing steel.

Figure 8 illustrates the relative susceptibility to temper embrittlement of the various steels as indicated by the difference in transition temperature between the E and R conditions. Figure 9 illustrates the reduction in temper-embrittlement index (ΔTT) produced by the addition of rare-earths.

OPTICAL METALLOGRAPHY

Figure 10 shows the etched microstructures of steels A1, A3, V1 and V2. The structure of steel A2 was essentially indentical to that of A3. Figure 11 shows the appearance of the inclusions in the RE-bearing steels.

QUANTITATIVE METALLOGRAPHY

The quantitative television microsope (QTM) was used to determine inclusion volume fraction (equal to area fraction), size, aspect ratio and number of inclusions per unit area for steels A1, A3, V1 and V2. Average values ($\bar{X}$) and standard deviations (S) were obtained for 5 or 6 scans of 20 fields of 0.0102245 mm^2 area for all except steel V2. For V2, the aspect ratio function was non-operational for all but one scan. A value lower than unity for the one scan indicated that the specimen was oriented incorrectly. A further scan of 60 fields of 0.0156645 mm^2 area confirmed this, and indicated a aspect ratio of 1.93/1.85. Size values for the original scans of V2 were, therefore, corrected by this ratio.

The results of the inclusion measurements are recorded in Table 4. Figure 12 shows the distribution of inclusions in various size ranges and Fig. 13 shows the cumulative numbers of inclusions bigger than size limits from 4 μm to 10 μm.

DISCUSSION

All the experimental steels, with the exception of A1, had higher-than-normal contents of phosphorus and silicon. Phosphorus was added so that the embrittlement treatment would result in a significant increase in the impact transition temperature. Because of the high phosphorous contents, the required content of rare-earths was very high. Rare-earths were added as RESi, resulting in high silicon contents, so silicon was added to the other steels to make their compositions comparable with the rare-earth-bearing steels.

The high silicon content had significant consequences on the impact toughness, inclusion content and microstructure. It resulted in a 50 to 70°C increase in the transition temperature in the retoughened condition (Fig. 4). Because of a shift of the ferrite nose of the CCT curve to shorter elapsed transformation times, the composition was borderline for development of the desired ferrite-free, bainite microstructure. This is demonstrated by the presence of some pro-eutectoid ferrite in V1 (Fig. 10). Previous work on the air-melted steels (5) indicated that air-cooling from the austenitizing temperature resulted in considerable quantities of ferrite. Comparison of the rare-earth-free steel shows that V1 has many more inclusions, especially those smaller than 2 μm, with a smaller average inclusion size, than A2. This is obviously attributable to the higher silicon content of V1, rather than vacuum-melting.

As shown by Fig. 5, vacuum-melting resulted in a 20°C improvement in the impact transition temperature. Comparison of steels A3 and V2 showed that vacuum-melting results in fewer inclusions, particularly in sizes smaller than 2 μm, and a slightly larger inclusion size.

The addition of rare-earths causes a 45°C increase in the transition temperature (Fig. 6) and a significant decrease in the upper-shelf energy (Fig. 1). Figure 10, as well as earlier results (5), indicates that the addition of rare-earths tends to suppress ferrite formation. It also results in a very large increase in the number and volume fraction of inclusions, which is obviously the reason for the drop in upper-shelf energy.

The foregoing remarks refer to properties in the retoughened condition. Temper embrittlement effects are demonstrated by changes in properties resulting from the embrittlement treatment. Table 1 indicates that embrittlement

does not result in any significant change in tensile properties. Figure 8 shows the changes in impact transition temperature (index of temper embrittlement) for the experimental steels. Hardly any embrittlement is developed by the low-phosphorus steel (A1), whereas substantial embrittlement is produced in the rare-earth-free steels A2 and V1 (80 to 90°C, and 100 to 120°C, respectively). Figure 14 shows that steels A1, V1 and A2 developed a degree of embrittlement close to that predicted by their J factors (3). Thus, the value of low impurity contents for minimizing temper embrittlement is readily apparent.

The rare-earth-treated steels exhibited substantially reduced degrees of temper embrittlement (Figs. 8 and 14). The air-melted steel (A3) showed a 50 to 70°C shift in transition temperature, and the vacuum-melted steel (V2) showed 30 to 60°C of embrittlement. Figure 9 indicates that, while not eliminating temper embrittlement, rare-earths reduce it substantially, and are twice as effective for vacuum-melted steel as for air-melted steel.

CONCLUSIONS

1. High-purity (low phosphorus) 2-1/4 Cr-1Mo steel develops relatively little temper embrittlement. The steel tested displayed the best impact properties of all the experimental steels in the retoughened condition.
2. Vacuum-melted steels had better impact properties in the retoughened condition than did air-melted steels of similar composition.
3. Phosphorus-doped 2-1/4 Cr-1Mo steel develops a substantial degree of temper embrittlement.
4. The degree of embrittlement displayed by the experimental steels without rare-earths is linearly related to their J factors.
5. Rare-earth additions to phosphorus-doped 2-1/4 Cr-1Mo steel, while not eliminating temper embrittlement, do reduce it substantially. They are twice as effective in vacuum-melted steel as in air-melted steel, presumably because the rare-earth addition is protected from oxidation.
6. The large additions of rare earths required because of the very high phosphorus content of these steels, results in a large increase in the number and volume fraction of inclusions and a consequent substantial decrease in the upper-shelf energy.

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Table 1 - Chemical composition (wt %)

Element	ASTM A542	A1	A2	A3	V1	V2
C	0.15 max	0.12	0.10	0.12	0.10	0.12
Mn	0.3/0.6	0.47	0.50	0.53	0.49	0.50
Si	0.50 max	0.37	0.56	0.48	0.58	0.50
S	0.035 max	0.005	0.005	0.002	0.009	0.005
P	0.035 max	0.005	0.038	0.039	0.032	0.034
Sn	-	0.001	0.001	0.001	0.001	0.001
Al	-	0.003	0.050	0.038	0.086	0.072
Cr	2.0/2.5	2.33	2.13	2.29	2.43	2.40
Mo	0.9/1.1	1.01	1.01	0.98	1.05	1.05
Ce	-	-	-	0.115	-	0.117
La	-	-	-	0.057	-	0.064

Table 2 - Tensile properites of vacuum-melted steels

Property	V1E	V1R	V2E	V2R
UTS (MPa)	729	704	725	716
YS (MPA)	613	598	719	625
Y/U	0.84	0.85	0.85	0.88
El, % ($4\sqrt{A}$)	30.0	28.5	26.0	26.0
R.A., %	74.5	85.0	69.5	70.0

Table 3 - Impact properties (J)

Test Temp. (°C)	Steel - Condition - Orientation													
	A1EL	A1RL	A2EL	A2RL	A3EL	A3RL	V1EL	V1RL	V1ET	V1RT	V2EL	V2RL	V2ET	V2RT
+ 80					101									
+ 60			114		93	115	104		146		107	114	82	86
+ 40			92		83	115	86		117					
+ 30					68									
+ 20	182	190	95	162	58	114	95	208	102	202	105	116	78	81
+ 10			77				64		82		73		64	
+ 5			56		41						84			
- 10	184	192	22	143	32	89	42				69		49	
- 20			26			91	31	218	48	170	49	110	42	84
- 35						47								
- 40	171	161	23	136	10	29	10	140		156		54		65
- 50				102		43					26	91	24	48
- 60	180	176		71				114	27	94		42		40
- 70				84				93				36		
- 80	174	160		61				96		47				
-100	58	138		10				64		47				
-120	82	109												
-140	28	27												

Table 4 - QTM inclusion measurement data

Measurement	A1		A3		V1		V2	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
Volume % 0.085	0.047	0.261	0.069	0.057				
0.010 0.248	0.045							
Average diam.(μ)	2.39	0.35	1.70	0.09				
1.09 0.08	1.88	0.11						
Aspect ratio	1.22	0.08	1.09	0.05				
1.03 0.02	-	-						
Inclusions/mm^2	195	65	1049	242	468	142	655	145

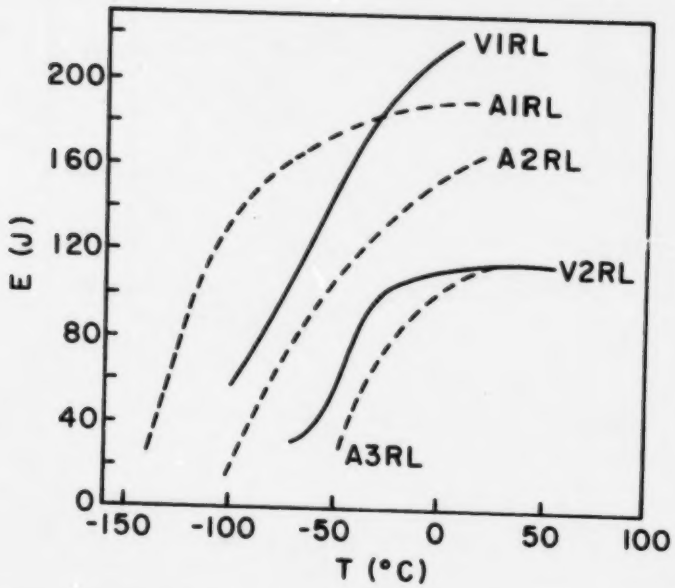


Fig. 1. Impact properties in "retoughened" condition (Solid-vacuum; dashed-air). (neg 7848)

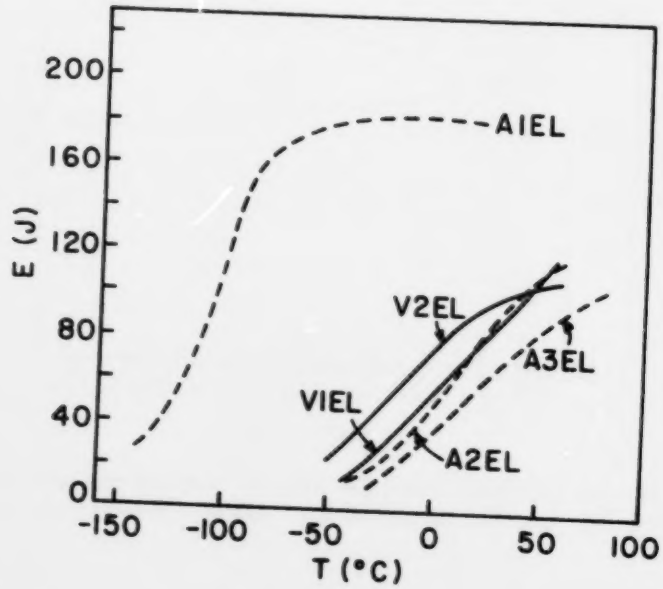


Fig. 2. Impact properties in "embrittled" condition (Solid-vacuum; dashed-air). (neg 7847)

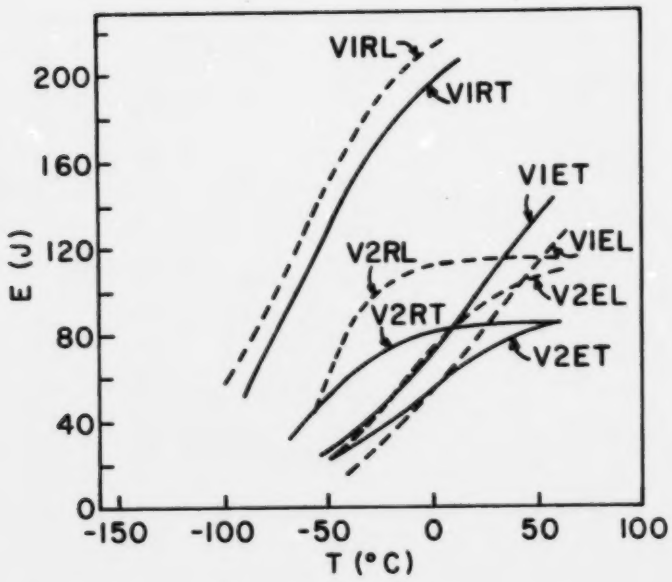


Fig. 3. Comparison of transverse (solid) and longitudinal (dashed) orientations or vacuum-melted steels. (neg 7838)

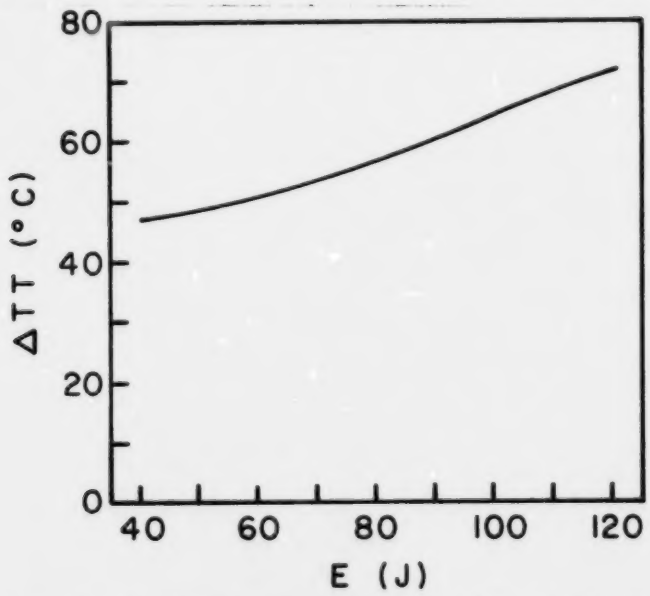


Fig. 4. Increase in transition temperature owing to high levels of P and Si (A2RL vs A2RL). (neg 7842)

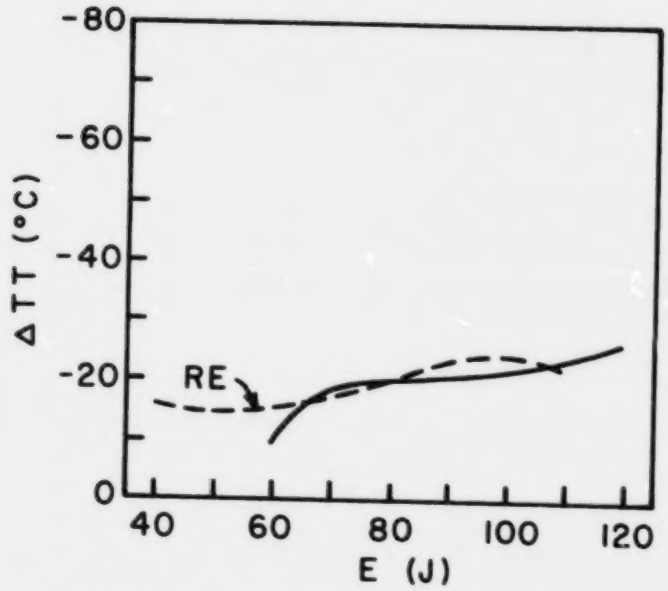


Fig. 5. Decrease in transition temperature owing to vacuum-melting (V1RL va A2RL and V2RL vs A3RL). (neg 7845)

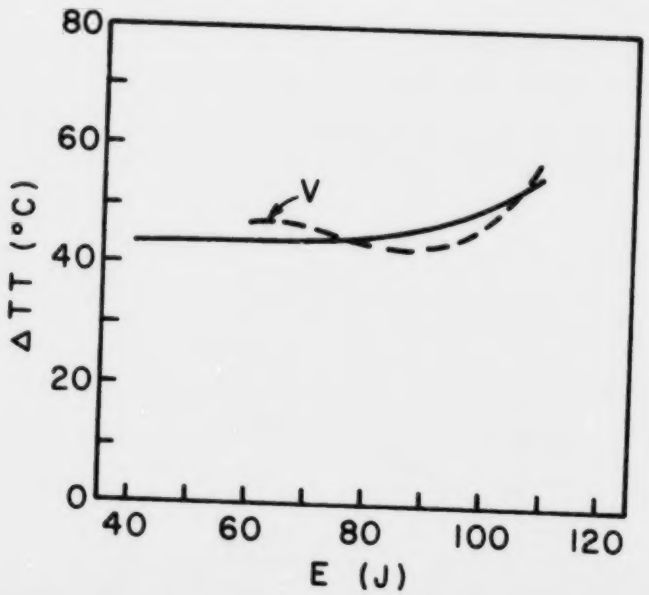


Fig. 6. Increase in transition temperature owing to rare-earth addition (A3RL vs A2RL and V2RL vs V1RL). (neg 7840)

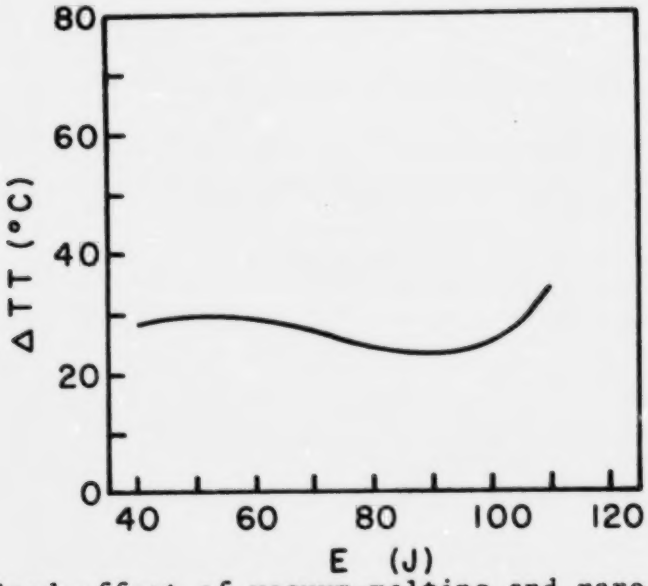


Fig. 7. Combined effect of vacuum-melting and rare-earth addition (V2RL). (neg 7843)

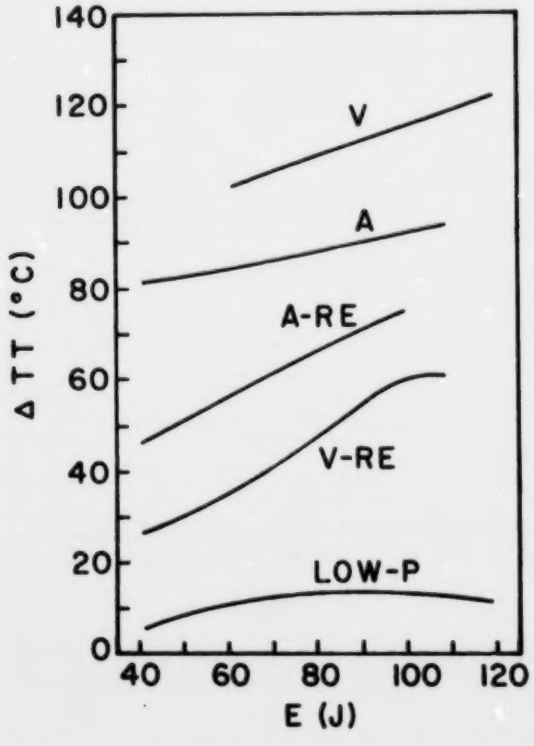


Fig. 8. Susceptibility to temper embrittlement of the experimental steels. (neg 7844)

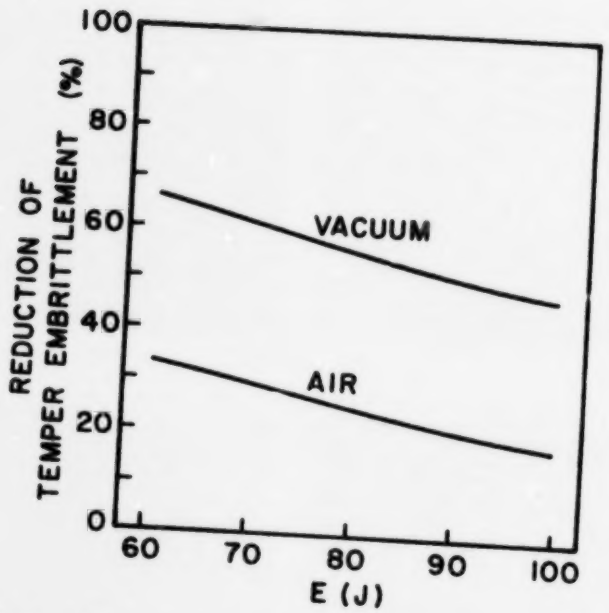
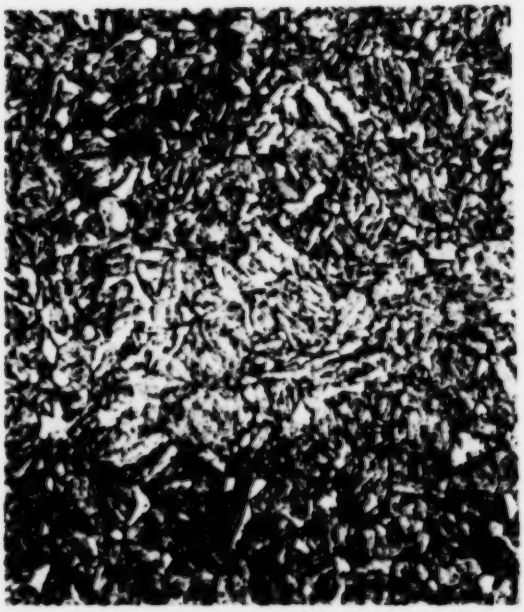


Fig. 9. Reduction of temper-embrittlement index (ΔATT) owing to the addition of rare-earths. (neg 7846)

A1 (neg 7858)

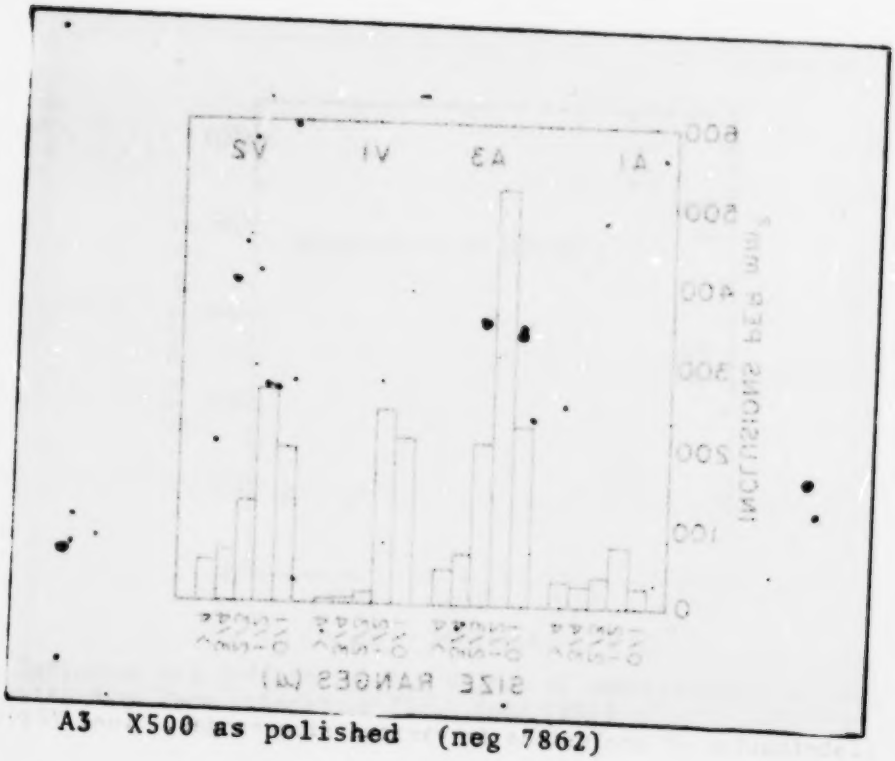
A3 (neg 7859)

V1 (neg 7860)



V2 (neg 7861)

Fig. 10. Microstructures of experimental steels. (All X500 etched 30 s., 2% nital).



A3 X500 as polished (neg 7862)

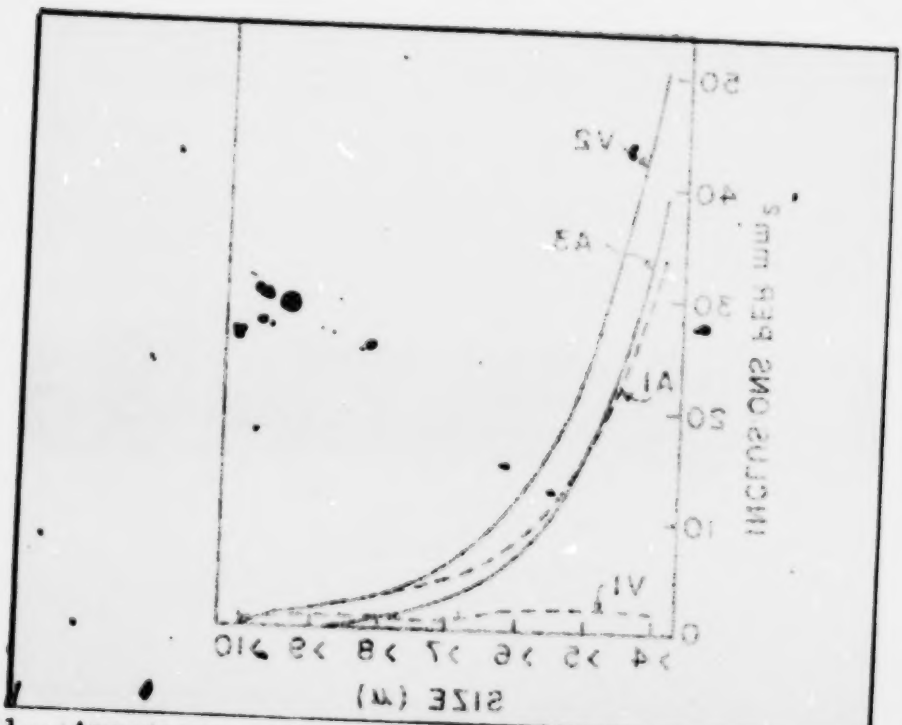


Fig. 11: Appearance of inclusions in RE bearing steels.

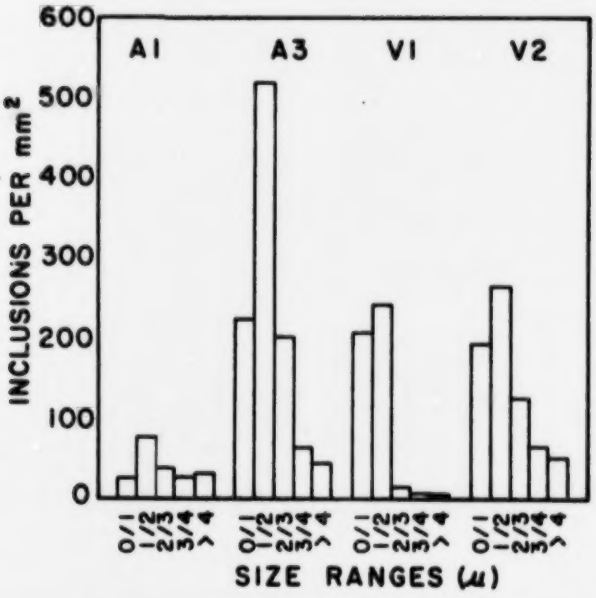


Fig. 12 Distribution of inclusions in various size ranges. (neg 7839)

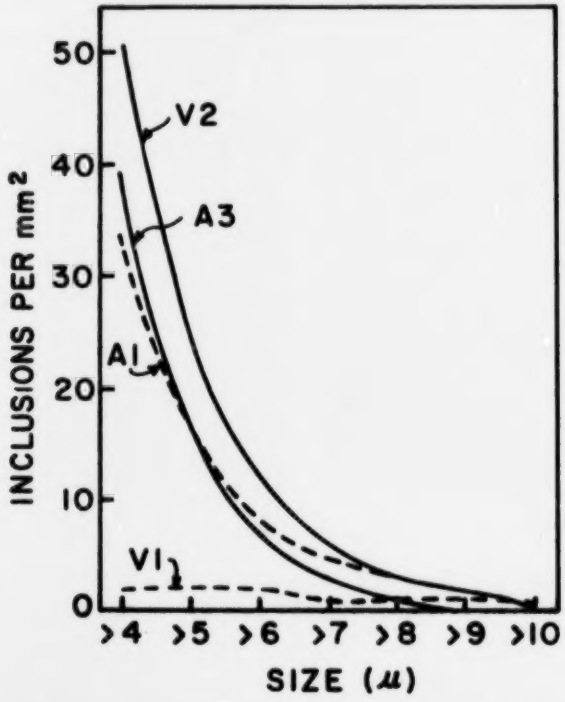


Fig. 13. Cumulative number of inclusions bigger than sizes shown. (neg 7837)

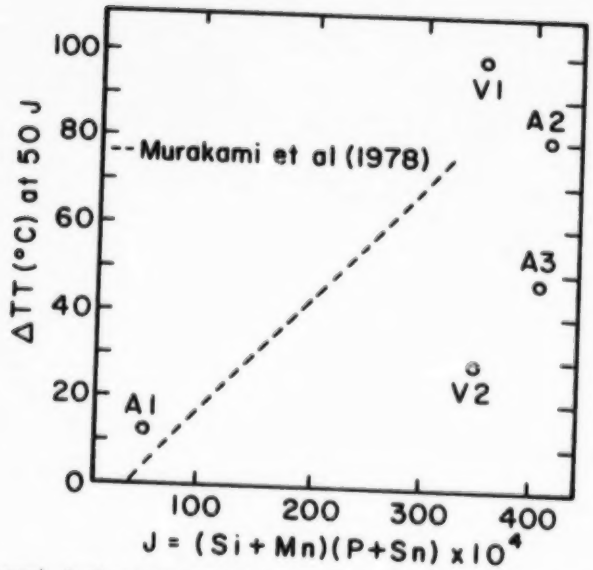


Fig. 14 Influence and J-factor on the degree of embrittlement as compared with data from literature (3). (neg 7841)